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(71) Applicant
Kodak Limited (United Kingdom),
Kodak House, Station Road, Hemel Hempstead,
Hertfordshire

(72) Inventor
Paul William Law

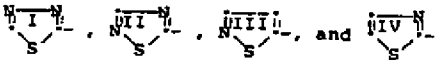
(74) Agent and/or Address for Service
P A C Baron, I E Davis, R F Nunney,
Kodak Limited, Patent Department, Headstone Drive,
Harrow, Middx HA1 4TY

(54) Disperse and acid azo dyes having 1,2-dihydroquinoline couplers and heterocyclic diazos

(57) New dyes of formula (I) give blue to green shades on polyamide fibres:

D–N = N–C′ (I)

wherein C′ is an optionally substituted 1,2-dihydroquinoline coupler, and D is selected from:



wherein rings I–IV are optionally substituted.

GB 2 148 918 A

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SPECIFICATION

Disperse and acid azo dyes having 1,2-dihydroquinoline couplers and heterocyclic diazos

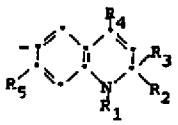
This invention concerns disperse and acid dyes particularly suited for the dyeing of polyamide fibres, and having the general formula

$$D - N = N - C^1$$

wherein D is thiazol-2-yl, isothiazol-3-yl, 1,2,4-thiadiazol-5-yl or 1,3,4-thiadiazol-2-yl, each of which is unsubstituted or substituted with substituents such as acyl, acylamido, alkyl, SO_3M, carboalkoxy, halogen, cyano and alkyl-SO_3M, as defined below, and C^1 is a 1,2-dihydroquinoline coupler which is unsubstituted or substituted with such substituents as alkyl, aryl, alkyl-SO_3M, and substituted alklyl.

More particularly, with regard to the above formula, D is selected from

wherein the rings I–IV are either unsubstituted or substituted with substituents selected from alkyl, alkoxy, halogen, alkylsulfonyl, SO_2NH_2, $SO_2NHalkyl$, SO_3M, alkyl-SO_3M, $SO_2N(alkyl)_2$, arylsulfonyl, acylamido, aryl, arylthio, alkenylthio, cyclohexylthio, $SO_3C_6H_5$, cyano, thiocyano, cyclohexylsulfonyl, alkylthio, nitro, formyl, alkanoyl, alkoxycarbonyl, aroyl, dialkylcarbamoyl, aroylamino alkylsulfonamido, CF_3, carbamoyl, alkylcarbamoyl, and cyclohexyl, wherein the alkyl, alkenyl and cyclic moieties in said ring substituents may bear up to three substituents different from the moiety and independently selected from hydroxy, alkyl, alkoxy, aryl, cyclohexyl, furyl (C_4H_3O), aroyloxy, alkoxycarbonyl, alkanoyloxy, SO_2NH_2, $SO_2NHaryl$, $SO_2NHalkyl$, SO_2N-(alkyl)$_2$, NHCOOalkyl, NHCONHalkyl, acylamido, alkylsulfonamido, succinimido ($C_4H_4O_2N$), alkyl-SO_3M, glutarimido ($C_5H_6O_2N$), phthalimido ($C_8H_4O_2N$), 1-(2-pyrrolidono) (C_4H_6ON), cyano, $CONH_2$, CONHalkyl, $CON(alkyl)_2$, alkoxy-alkoxy, alkylthio, halogen, arylthio, alkylsulfonyl, arylsulfonyl, and aryloxy, and the coupler C^1 has the formula



wherein R_1 is H or a group selected from alkyl, aryl and cyclohexyl, which groups may themselves be substituted with 1–3 substituents different from the said group and independently selected from hydroxy, alkoxy, aryl, aryloxy, cyclohexyl, cyclohexoxy, furyl (C_4H_3O), aroyloxy, alkoxycarbonyl, alkanoyloxy, SO_2NH_2, $SO_2NHaryl$, $SO_2NHalkyl$, SO_2N-(alkyl)$_2$, NHCOOalkyl, NHCONHalkyl, acylamido, alkylsulfonamido, succinimido ($C_4H_4O_2N$), glutarimido ($C_5H_6O_2N$), phthalimido ($C_8H_4O_2N$), 1-(2-pyrrolidono) (C_4H_6ON), cyano, $CONH_2$, CONHalkyl, -SO_3M, alkyl-SO_3M, $CON(alkyl)_2$, alkoxyalkoxy, alkylthio, halogen, arylthio, alkylsulfonyl and arylsulfonyl, R_2 and R_3 are each independently selected from H and alkyl, R_4 is H, alkyl or alkyl-SO_3M, and R_5 is selected from H, alkyl, alkoxy, alkenyl of 2–6 carbons, halogen, acylamido, alkylthio and formamido, wherein the alkyl moieties thereof may be substituted with 1–3 substituents independently selected from hydroxy, halogen, cyano, alkoxy, alkylthio, alkanoyl, alkanoyloxy, and alkoxycarbonyl, wherein M is selected from H, Na, K, NH_4, $\frac{Ca}{2}$, $\frac{Zn}{2}$ and the colorless cations of primary, secondary and tertiary aliphatic and aryl amines.

The various alkyl moieties in, for example, alkoxy, alkanoyl and the like within the above definitions of R_1, R_5, and the D radical substituents preferably have 1–6 carbons, and they and the alkenyl groups are straight or branched chain. Any aryl moiety preferably has 6–10 ring carbon atoms.

Preferred of the present dyes are where the substituents on the D rings are selected from alkylthio, arylthio, cyclohexylthio, alkyl-SO_3M, cyanoalkyl, alkyl and halogen, R_1 is H, alkyl,

hydroxyalkyl, alkanoyloxyalkyl or alkoxycarbonylalkyl, and R_5 is H or alkyl.

The dyes of this invention impart blue to green shades on fibers, particularly polyamides, exhibiting improvements in fastness to one or more of light, ozone, perspiration, oxides of nitrogen, washing, sublimation and crocking, leveling, transfer, pH stability, exhaustion, build and diminished red flaring.

The diazo components used in this invention are prepared according to procedures well known to the art. The present disperse dyes may be applied to polyamide fibers by conventional dyeing procedures, e.g., dispersed in a lignin sulfonate and dyed at 98°C. on nylon fabric for one hour from an aqueous bath.

The acid dyes of the invention may be applied to polyamide fiber by the following method:

The test dye, as a mixture with a sulphate such as ammonium sulfate, is pasted with boiling water and then made up to a known volume with water to give a weight ratio of water to dye of 30:1. Four percent on weight of fiber (owf) of a lignin sulphonate leveling agent is added, followed by ammonium acetate (about 3.0% owf) to adjust the pH to 6. The initial dyeing temperature is 40°C. which is raised to the final dyeing temperature of 98°C. over 30 minutes. The dye bath is held at 98°C. for 60 minutes, then cooled, and the test fabric given a warm water rinse and air drying.

The following examples illustrate procedures which are generally applicable for preparation of the present couplers and dyes.

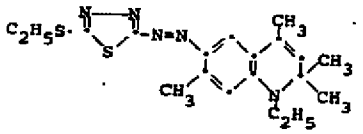
EXAMPLE 1

(a)—*Preparation of 1,2-Dihydro-2,2,4,7-Tetramethylquinoline*

Meta-toluidine (535 g.) and iodine (6 g.) are charged to a 2 liter, 3 neck, round bottom flask. The reaction is heated to 155°C. and about 3,500 g. of acetone is added at 155–160°C. beneath the surface over a 12 hour period. A mixture of acetone and water distills off during the addition. The reaction mixture is heated one-half hour at 160°C. and then distilled to leave about 690 g. of 1,2-dihydro-2,2,4,7-tetramethylquinoline boiling at 107–111°C. at 0.55 mm., a 74% yield. This product is then ethylated with triethylphosphate in the presence of ethyl iodide.

(b)—*Diazotization and Coupling*

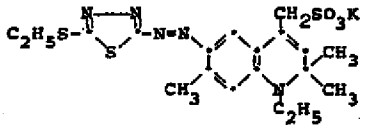
Sodium nitrite (3.6 g.) is added portionwise to 25 ml. of concentrated H_2SO_4. The solution is cooled and 100 ml. of 1:5 acid (1 vol. propionic:5 vol. acetic) is added below 15°C. The mixture is cooled and 8.05 g. (0.05 m) of 2-amino-5-ethylthio-1,3,4-thiadiazole is added below 10°C. After stirring at 0–5°C. for one hour, the diazo solution is added to 1-ethyl-2,2,4,7-tetramethyl-1,2-dihydroquinoline (10.75 g., 0.05 mole) in 50% aqueous ethanol (54.0 cc.) containing sodium acetate (2.05 g), at <5°C. After stirring at 0–5°C. for one hour the dye is warmed to room temperture and precipitated by adding to cold water. The product is filtered and washed well with water to yield the dye.



The preparation of the sulfonated 1,2-dihydro-quinoline is given in German Offen. 3,005,874 (C.A. *94*, 15593K, 1981) and comprises sulfonating the 4-alkyl-1,2-dihydroquinoline with H_2SO_4, $ClSO_3H$, and/or SO_3 and converting, if desired, the acid group to its salt in known manner.

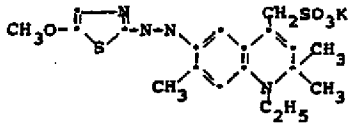
EXAMPLE 2

The diazonium from Example 1(b) is added to the potassium salt of 1-ethyl-2,2,7-trimethyl-1,2-dihydroquinoline-4-yl methyl sulfonic acid (0.01 mole) in water (11 cc.) at <5°C. After stirring at 0–5°C. for one hour the dye was warmed to room temperature and precipitated by adding to a saturated potassium chloride solution. The product was filtered and washed with diethyl ether, to yield the final dye product.



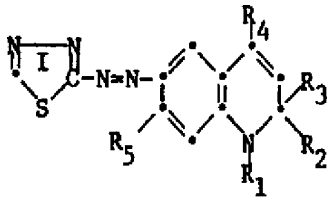
EXAMPLE 3

By application of the above procedure, in Example 2, the following dye is prepared

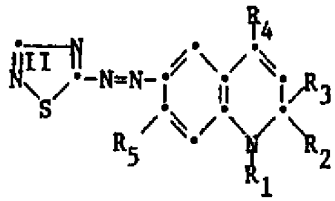


The exemplary dyes of the following tables are prepared as in the above examples by procedural modifications if such are needed, as known to those skilled in the art.

TABLE 1



and



Substituent on Ring I or II	R_5	R_2	R_3	R_4	R_1
None	H	H	H	H	H
None	H	H	CH_3	CH_3	C_2H_5
CN	CH_3	CH_3	CH_3	CH_3	C_3H_7-n
CH_3	CH_2CH_2OH	CH_3	CH_3	CH_2SO_3K	C_4H_9-n
$CH_2CH_2SCH_3$	CH_2Cl	H	$CH(CH_3)_2$	CH_3	CH_2CH_2-$SO_2NHC_6H_5$
$CH_2CH_2OCH_2CH_2OC_2H_5$	OCH_2Cl	H	CH_3	CH_2SO_3Na	$CH_2CH_2OC_6H_5$
$CH_2CH(CH_3)_2$	OCH_3	H	N	H	CH_3
C_6H_4-p-SO_3K	OCH_3	H	H	$CH_2SO_3(Ca/2)$	C_6H_4-p-SO_3K
C_6H_{11}	CH_2CH_2CN	H	H	$CH_2SO_3(Zn/2)$	C_6H_{11}
C_6H_4-o-Cl	Cl	H	CH_3	CH_3	$CH_2CH_2OC_6H_{11}$
C_6H_4-m-CH_3	Cl	H	CH_3	$CH_2SO_3NH_4$	$CH_2CH_2SO_2NH_2$
C_6H_4-p-OCH_3	H	H	CH_3	CH_3	CH_2CH_2OH

OC_2H_5	OCH_3	CH_3	CH_3	CH_3	$CH_2CH_2SO_2N(C_2H_5)_2$
$CH_2SO_2NHCH_3$	NHCHO	CH_3	CH_3	CH_3	$CH_2CH_2OC_2H_5$
$CH_2SO_2NH_2$	$NHCOCH_2OCCH_3$	C_4H_9-n	C_4H_9-n	CH_3	CH_2CN
CH_2OOCCH_3	$NHCOCH_2CH_3$	C_4H_9-n	C_4H_9-n	H	CH_2CONH_2
CH_2COOCH_3	$NHCOC_2H_5$	C_4H_9-n	C_4H_9-n	H	$CH_2CONHCH_3$
$CH_2OOCC_6H_5$	$NHCOC_6H_5$	C_3H_7-n	C_3H_7-n	$CH_2CH_2SO_3K$	$CH_2CON(C_2H_5)_2$
SO_2NHCH_3	$NHCOC_2H_5$	C_3H_7-n	C_3H_7-n	H	$CH_2NHCOCH_3$
$CH_2CON(C_2H_5)_2$	$NHCOC_6H_{11}$	C_3H_7-n	C_3H_7-n	CH_2SO_3N H(Et)$_3$	$CH_2NHCOOCH_3$
Cl	H	CH_3	CH_3	H	CH_2OOCCH_2-SO_3K
$CH_2CH_2(C_4H_3O)$	CH_2SCH_3	H	CH_3	CH_2SO_3N $HCH_3(Ph)_2$	$CH(C_4H_6ON)$
$SO_2C_6H_{11}$	$CH_2CH{=}CH_2$	H	H	H	$CH_2CH_2COOCH_3$
I	Br	H	CH_3	CH_3	$CH_2CH_2COOCH_3$
Br	I	H	CH_3	CH_3	H
SO_2CH_3	F	H	CH_3	CH_2SO_3K	$CH_2CH_2C_2H_5$
SO_2NH_2	SCH_3	H	CH_3	CH_3	C_3H_7-n
$SO_2NHCH_2SO_3K$	CH_2OOCCH_3	H	CH_3	CH_3	C_2H_5

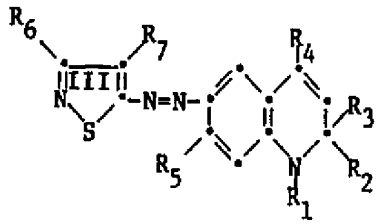
$SO_2N(C_2H_5)_2$	OCH_3	H	CH_3	CH_3	$CH_2CH_2C_6H_5$
$SO_2NHCH_2CH_2CH_2OCH_3$	CH_3	H	CH_3	CH_3	$CH_2C_6H_{11}$
$SO_2CH_2CH_2OC_2H_5$	CH_3	H	CH_3	CH_3	CH_2Cl
SC_6H_5	$CH_2CH_2COOCH_3$	H	CH_3	CH_3	C_6H_5
SC_6H_{11}	$CH_2CH(OH)CH_2OH$	H	CH_3	CH_3	C_6H_4-p-OCH_3
$SO_2C_6H_5$	CF_3	H	CH_3	CH_3	C_6H_{10}p-OH
$SO_3C_6H_5$	CF_3	H	CH_3	CH_3	$CH_2CH_2SC_6H_5$
SCH_2CH_2OH	H	CH_3	CH_3	CH_3	$CH_2CH_2SO_2CH_3$
$SCH_2CH{=}CH_2$	H	CH_3	CH_3	CH_3	$CH_2CH_2SO_2C_6H_5$
$SCH_2COOC_2H_4$-SO_3K	$CH_2CH(Cl)CH_2Cl$	CH_3	CH_3	CH_3	$CH_2CH_2OCH_2CH_2OC_2H_5$
$SCH_2C_6H_5$	$CH_2CH(OCH_3)CH_2OCH_3$	CH_3	CH_3	CH_3	CH_2CN
$SCH_2C_6H_{11}$	CH_3	CH_3	CH_3	CH_2SO_3K	$CH_2(C_8H_4O_2N)$
$SCH_2CH_2OC_2H_5$	CH_3	CH_3	CH_3	CH_3	$CH_2CONHCH_3$
SCN	H	CH_3	CH_3	CH_3	$CH_2CON(C_2H_5)_2$
$SCH_2CH_2NHCOCH_3$	H	CH_3	CH_3	CH_2SO_3Na	$CH_2NHCOCH_3$
$SCH_2CH_2(C_4H_4O_2N)$	CH_3	CH_3	CH_3	CH_3	$CH_2NHCOOCH_3$
$CH_2SC_6H_5$	CH_2CH_2OH	CH_3	CH_3	CH_3	CH_2OOCCH_3

$CH_2CH_2SO_2CH_3$	CH_2Cl	CH_3	CH_3	CH_3	$CH_2(C_4H_6O_2N)$
$CH_2SO_2C_6H_5$	OCH_2Cl	CH_3	CH_3	H	$CH_2CH_2COOCH_3$
$SCH_2CH_2OC_6H_5$	OCH_3	CH_3	CH_3	H	$CH_2CH_2COOCH_3$
SCH_2CH_3	OCH_3	CH_3	CH_3	C_3H_7-n	$CH_2OOCC_6H_5$
$CH_2(C_8H_4O_2N)$	CH_2CH_2CN	CH_3	CH_3	C_3H_7-n	C_2H_5
$CH_2NHCONHCH_3$	Cl	CH_3	CH_3	C_2H_5	C_2H_5
$CH_2NHCOOCH_3$	H	CH_3	CH_3	C_2H_5	C_2H_5
$CH_2SO_2NHC_6H_5$	OCH_3	CH_3	CH_3	CH_3	C_2H_5
$CH_2SO_2N(C_2H_5)_2$	NHCHO	H	H	H	CH_3
SCH_3	$NHCOCH_2OCCH_3$	H	H	H	C_6H_5
$CH_2(C_4H_4O_2N)$	$NHCOCH_2CH_2OCH_3$	CH_3	CH_3	CH_3	C_6H_{11}
$CH_2SO_2NHCH_3$	$NHCOC_2H_5$	CH_3	CH_3	CH_2SO_3K	C_2H_5
$CH_2CH_2NHCOCH_3$	$NHCOC_6H_5$	CH_3	CH_3	CH_3	CH_2CH_2OH
$NHCOCH_3$	$NHCOC_2H_5$	CH_3	CH_3	CH_3	CH_2CH_2OH
$CH_2CH_2(C_4H_6ON)$	$NHCOC_6H_{11}$	CH_3	CH_3	CH_2 SO_3NH_4	CH_2CH_2OH
C_6H_4-p-CN	H	CH_3	CH_3	CH_3	$CH_2CH_2OC_2H_5$
CH_2CONH_2	CH_2SCH_3	CH_3	CH_3	CH_3	CH_2CN

$CH_2CONHCH_3$	$CH_2CH{=}CH_2$	CH_3	CH_3	CH_3	CH_2CONH_2
NO_2	H	H	H	H	H
CHO	H	H	CH_3	CH_3	C_2H_5
$COCH_3$	CH_3	CH_3	CH_3	CH_3	C_2H_5
$COOCH_3$	CH_2CH_2OH	CH_3	CH_3	CH_3	C_2H_5
COC_6H_5	CH_2Cl	H	$CH(CH_3)_2$	CH_3	C_2H_5
$NHCOC_6H_5$	OCH_2Cl	H	CH_3	$CH_2SO_3NH_4$	C_2H_5
$NHSO_2CH_3$	OCH_3	H	N	H	CH_3
CF_3	OCH_3	H	H	$CH_2CH_2SO_3K$	C_6H_5
$CONH_2$	CH_2CH_2CN	H	H	H	C_6H_{11}
$CONHCH_3$	Cl	H	CH_3	CH_2SO_3K	C_2H_5
$CON(C_2H_5)_2$	Cl	H	CH_3	CH_3	CH_2CH_2OH
SCH_2CH_3	H	H	H	H	C_2H_5
C_6H_5	CH_3	CH_3	CH_3	CH_3	C_2H_5
Cl	CH_3	CH_3	CH_3	H	$CH_2CH_2C_6H_5$
CH_3	CH_3	CH_3	CH_3	H	C_2H_5
C_6H_5	CH_3	CH_3	H	H	CH_2CH_2OH

SCH_2CH_3	CH_3	CH_3	CH_3	$CH_2C_6H_5$
SCH_2CH_3	H	H	$CH_2SO_3NH_4$	C_2H_5
C_6H_5	CH_3	CH_3	CH_2SO_3Na	C_2H_5
Cl	CH_3	CH_3	CH_2SO_3Na	$CH_2CH_2C_6H_5$
CH_3	CH_3	CH_3	CH_2SO_3Na	C_2H_5
C_6H_5	CH_3	H	$CH_2SO_3NHEt_3$	CH_2CH_2OH
SCH_2CH_3	CH_3	H	CH_2SO_3K	$CH_2C_6H_5$

TABLE 2



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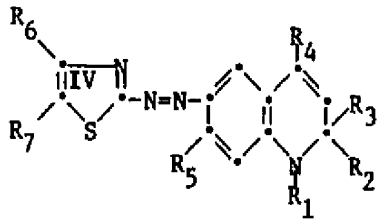


R_6	R_7	R_5	R_2	R_3	R_4	R_1
H	H	H	H	H	H	H
H	H	H	H	CH_3	CH_3	C_2H_5
Cl	CN	CH_3	CH_3	CH_3	CH_3	C_2H_5
Br	CH_3	CH_2CH_2OH	CH_3	CH_3	CH_3	$CH_2CH_2SO_2N(CH_3)_2$
CH_3	$CH_2CH_2SCH_3$	CH_2Cl	H	$CH(CH_3)_2$	CH_2SO_3K	C_2H_5
CN	$CH_2CH_2OCH_2CH_2OC_2H_5$	OCH_2Cl	H	CH_3	$CH_2SO_3NH_4$	C_2H_5
C_2H_5	$CH_2CH(CH_3)_2$	OCH_3	H	N	H	$CH_2C_6H_4$-p-SCH_3
$COOCH_3$	C_6H_5	OCH_3	H	H	$CH_2SO_3(Ca/2)$	C_6H_5
$CONH_2$	C_6H_{11}	CH_2CH_2CN	H	H	H	C_6H_{11}
$CON(C_2H_5)_2$	C_6H_4-o-Cl	Cl	H	CH_3	$CH_2SO_3(Zn/2)$	C_2H_5
$CH_2OOC_2H_5$	C_6H_4-m-CH_3	Cl	H	CH_3	CH_3	CH_2CH_2OH
C_6H_5	C_6H_4-p-OCH_3	H	H	CH_3	CH_3	CH_2CH_2OH

$CH_2CH_2SCH_3$	OC_2H_5	OCH_3	CH_3	CH_3	CH_3	CH_2CH_2OH
$CH_2CH_2OCH_2CH_2OC_2H_5$	$CH_2SO_2NHCH_3$	NHCHO	CH_3	CH_3	CH_3	$CH_2CH_2OC_2H_5$
$CH_2CH(CH_3)_2$	$CH_2SO_2NH_2$	$NHCOCH_2OCCH_3$	C_4H_9-n	C_4H_9-n	CH_3	CH_2CN
C_6H_5	CH_2OOCCH_3	$NHCOCH_2CH_3$	C_4H_9-n	C_4H_9-n	H	CH_2CONH_2
C_6H_{11}	CH_2COOCH_3	$NHCOC_2H_5$	C_4H_9-n	C_4H_9-n	H	$CH_2CONHCH_3$
C_6H_4-o-Cl	$CH_2OOCC_6H_5$	$NHCOC_6H_5$	C_3H_7-n	C_3H_7-n	$CH_2CH_2SO_3K$	$CH_2CON(C_2H_5)_2$
C_6H_4-m-CH_3	SO_2NHCH_3	$NHCOC_2H_5$	C_3H_7-n	C_3H_7-n	H	$CH_2NHCOCH_3$
C_6H_4-p-OCH_3	$CH_2CON(C_2H_5)_2$	$NHCOC_6H_{11}$	C_3H_7-n	C_3H_7-n	CH_2SO_3Na	$CH_2NHCOOCH_3$
OC_2H_5	Cl	H	CH_3	CH_3	H	CH_2OOCCH_3
$CH_2SO_2NHCH_3$	$CH_2CH_2(C_4H_3O)$	CH_2SCH_3	H	CH_3	$CH_2SO_3N\ H(Et)_3$	$CH(C_4H_6ON)$
$CH_2SO_2NH_2$	$SO_2C_6H_{11}$	$CH_2CH=CH_2$	H	H	H	$CH_2CH_2COOCH_3$
CH_2OOCCH_3	I	Br	H	CH_3	CH_3	$CH_2CH_2COOCH_3$
$CH_2COOCH_2SO_3K$	Br	I	H	CH_3	CH_3	H
$CH_2OOCC_6H_5$	SO_2CH_3	F	H	CH_3	CH_2SO_3K	C_2H_5
SO_2NHCH_3	SO_2NH_2	SCH_3	H	CH_3	CH_3	C_2H_5
$CH_2CON(C_2H_5)_2$	$SO_2NHCH_2SO_3K$	CH_2OOCCH_3	H	CH_3	CH_3	C_2H_5
Cl	$SO_2N(C_2H_5)_2$	OCH_3	H	CH_3	$CH_2SO_3NH_4$	C_2H_5

$CH_2CH_2(C_4H_3O)$	$SO_2NHCH_2CH_2CH_2OCH_3$	CH_3	H	CH_3	CH_3	C_2H_5
$CH_2(C_8H_4O_2N)$	$SO_2CH_2CH_2OC_2H_5$	CH_3	H	CH_3	CH_3	CH_3
$CH_2NHCONHCH_3$	SC_6H_5	$CH_2CH_2COOCH_3$	H	CH_3	CH_3	C_6H_5
$CH_2NHCOOCH_3$	SC_6H_{11}	$CH_2CH(OH)CH_2OH$	H	CH_3	CH_3	C_6H_{11}
$CH_2SO_2NHC_6H_5$	$SO_2C_6H_5$	CF_3	H	CH_3	CH_2SO_3Na	C_2H_5
$CH_2SO_2N(C_2H_5)_2$	$SO_3C_6H_5$	CF_3	H	CH_3	CH_3	CH_2CH_2OH
SCH_3	SCH_2CH_2OH	H	CH_3	CH_3	CH_3	CH_2CH_2OH
$CH_2(C_4H_4O_2N)$	$SCH_2CH{=}CH_2$	H	CH_3	CH_3	CH_3	CH_2CH_2OH
$CH_2SO_2NHCH_3$	$SCH_2COOC_2H_5$	$CH_2CH(Cl)CH_2Cl$	CH_3	CH_3	CH_3	$CH_2CH_2OC_2H_5$
$CH_2CH_2NHCOCH_3$	$SCH_2C_6H_5$	$CH_2CH(OCH_3)CH_2OCH_3$	CH_3	CH_3	CH_3	CH_2CN
$NHCOCH_3$	$SCH_2C_6H_{11}$	CH_3	CH_3	CH_3	CH_3	CH_2CONH_2
$CH_2CH_2(C_4H_6ON)$	$SCH_2CH_2OC_2H_5$	CH_3	CH_3	CH_3	CH_2SO_3K	$CH_2CONHCH_3$
C_6H_4-p- CN	SCN	H	CH_3	CH_3	CH_3	$CH_2CON(C_2H_5)_2$
CH_2CONH_2	$SCH_2CH_2NHCOCH_3$	H	CH_3	CH_3	CH_3	$CH_2NHCOCH_3$
$CH_2CONHCH_3$	$SCH_2CH_2(C_4H_4O_2N)$	CH_3	CH_3	CH_3	CH_3	$CH_2NHCOOCH_3$
H	$CH_2SC_6H_5$	CH_2CH_2OH	CH_3	CH_3	CH_3	CH_2OOCCH_3
H	$CH_2CH_2SO_2CH_3$	CH_2Cl	CH_3	CH_3	CH_3	$CH_2(C_4H_6O_2N)$

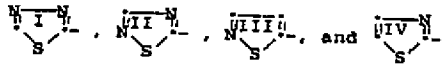
Cl	$CH_2SO_2C_6H_5$	OCH_2Cl	CH_3	CH_3	H	$CH_2CH_2COOCH_3$
Br	$SCH_2CH_2OC_6H_5$	OCH_3	CH_3	CH_3	H	$CH_2CH_2COOCH_3$
CH_3	SCH_2CH_3	OCH_3	CH_3	CH_3	C_3H_7-n	H
CN	$CH_2(C_8H_4O_2N)$	CH_2CH_2CN	CH_3	CH_3	C_3H_7-n	C_2H_5
C_2H_5	$CH_2NHCONHCH_3$	Cl	CH_3	CH_3	C_2H_5	C_2H_5
$COOCH_3$	$CH_2NHCOOCH_3$	H	CH_3	CH_3	C_2H_5	C_2H_5
$CONH_2$	$CH_2SO_2NHC_6H_5$	OCH_3	CH_3	CH_3	CH_3	C_6H_4-o,p-di-Cl
$CON(C_2H_5)_2$	$CH_2SO_2N(C_2H_5)_2$	NHCHO	H	H	H	CH_3
$CH_2OOC_2H_5$	SCH_3	$NHCOCH_2OCCH_3$	H	H	H	C_6H_5
C_6H_5	$CH_2(C_4H_4O_2N)$	$NHCOCH_2CH_2OCH_3$	CH_3	CH_3	CH_2SO_3K	C_6H_{10}-p-Cl
$CH_2CH_2SCH_3$	$CH_2SO_2NHCH_3$	$NHCOC_2H_5$	CH_3	CH_3	CH_3	C_2H_5
$CH_2CH_2OCH_2CH_2OC_2H_5$	$CH_2CH_2NHCOCH_3$	$NHCOC_6H_5$	CH_3	CH_3	CH_3	CH_2CH_2OH
$CH_2CH(CH_3)_2$	$NHCOCH_3$	$NHCOC_2H_5$	CH_3	CH_3	CH_2SO_3K	CH_2CH_2OH
C_6H_5	$CH_2CH_2(C_4H_6ON)$	$NHCOC_6H_{11}$	CH_3	CH_3	CH_3	CH_2CH_2OH
C_6H_{11}	C_6H_4-p-CN	H	CH_3	CH_3	CH_3	$CH_2CH_2OC_2H_5$
C_6H_4-o-Cl	CH_2CONH_2	CH_2SCH_3	CH_3	CH_3	CH_3	CH_2CN
C_6H_4-m-CH_3	$CH_2CONHCH_3$	$CH_2CH{=}CH_2$	CH_3	CH_3	CH_3	CH_2CONH_2

C_6H_4-p-OCH_3	NO_2	H	H	H	H	H
OC_2H_5	CHO	H	H	CH_3	CH_3	C_2H_5
$CH_2SO_2NHCH_3$	$COCH_3$	CH_3	CH_3	CH_3	CH_3	C_3H_7-n
$CH_2SO_2NH_2$	$COOCH_3$	CH_2CH_2OH	CH_3	CH_3	CH_3	C_4H_9-n
CH_2OOCCH_3	COC_6H_5	CH_2Cl	H	$CH(CH_3)_2$	CH_3	C_2H_5
CH_2COOCH_3	$NHCOC_6H_5$	OCH_2Cl	H	CH_3	CH_2SO_3K	C_2H_5
$CH_2OOCC_6H_5$	$NHSO_2CH_3$	OCH_3	H	N	H	CH_3
SO_2NHCH_3	CF_3	OCH_3	H	H	H	C_6H_5
$CH_2CON(C_2H_5)_2$	$CONH_2$	CH_2CH_2CN	H	H	H	C_6H_{11}
Cl	$CONHCH_3$	Cl	H	CH_3	$CH_2SO_3NH_4$	C_2H_5
$CH_2CH_2(C_4H_3O)$	$CON(C_2H_5)_2$	Cl	H	CH_3	CH_3	CH_2CH_2OH

CH_3	Cl	CH_3	CH_3	CH_3	CH_3	C_2H_5
CH_3	Br	H	CH_3	H	CH_3	CH_2CH_2OH
CH_3	CN	CH_3	CH_3	CH_3	CH_3	C_2H_5
CH_3	$COOCH_3$	CH_3	CH_3	H	CH_3	$CH_2CH_2OOCCH_3$
CH_3	$COOCH_3$	CH_3	CH_3	CH_3	CH_3	CH_2CH_2OH
H	SO_2CH_3	H	CH_3	H	CH_3	C_2H_5
H	CN	CH_3	H	H	CH_2	$CH_2CH_2OOCCH_3$
CH_3	Cl	CH_3	CH_3	CH_3	CH_2SO_3Na	C_2H_5
CH_3	Br	H	CH_3	H	CH_2SO_3Na	CH_2CH_2OH
CH_3	CN	CH_3	CH_3	CH_3	CH_2SO_3Na	C_2H_5
CH_3	$COOCH_3$	CH_3	CH_3	H	CH_2SO_3K	$CH_2CH_2OOCCH_3$
CH_3	$COOCH_3$	CH_3	CH_3	CH_3	CH_2SO_3K	CH_2CH_2OH
H	SO_2CH_3	H	CH_3	H	CH_2SO_3K	C_2H_5
H	CN	CH_3	H	H	CH_2SO_3K	$CH_2CH_2OOCCH_3$

CLAIMS

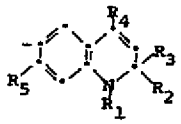
1. A dye of the formula D — N = N — C¹ wherein D is selected from



wherein the rings I–IV are either unsubstituted or substituted with substitutents selected from alkyl, alkoxy, halogen, alkylsulfonyl, SO_2NH_2, $SO_2NHalkyl$, $SO_2N(alkyl)_2$, arylsulfonyl, acylamido, aryl, arylthio, alkenylthio, cyclohexylthio, SO_3M, alkyl-SO_3M, $SO_3C_6H_5$, cyano, thiocyano, cyclohexyl-sulfonyl, alkylthio, nitro, formyl, alkanoyl, alkoxycarbonyl, aroyl, dialkylcarbamoyl, aroylamino, alkylsulfonamido, CF_3, carbamoyl, alkylcarbamoyl, and cyclohexyl, wherein the alkyl, alkenyl and cyclic moities in said ring substituents may bear up to three substituents different from the moiety and independently selected from hydroxy, alkyl, alkoxy, aryl, SO_3M, alkyl-SO_3M, cyclohexyl, furyl, (C_4H_3O), aroyloxy, alkoxy carbonyl, alkanoyloxy, SO_2NH_2, SO_2N-Haryl, SO_2NH-alkyl, $SO_2N(alkyl)_2$, NHCOOalkyl, NHCONHalkyl, acylamido, alkysulfonamido, succinimido ($C_4H_4O_2N$), glutarimido ($C_5H_6O_2N$), phthalimido ($C_8H_4O_2N$), 1-(2-pyrrolidono) (C_4H_6ON), cyano, $CONH_2$, CONHalkyl, CON-$(alkyl)_2$, alkoxyalkoxy, alkylthio, halogen, arylthio, alkylsulfonyl, arylsulfonyl, and aryloxy wherein M is selected from H, Na, K, NH_4, $\frac{Ca}{2}$, $\frac{Zn}{2}$

and the colorless cations of salts of primary, secondary and tertiary aliphatic and aryl amines, and wherein C^1 is a substituted or unsubstituted 1,2-dihydroquinoline radical.

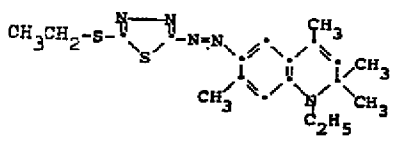
2. A dye according to Claim 1 wherein the coupler C has the formula



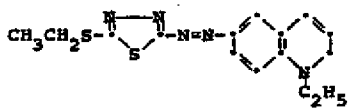
wherein R_1 is H or a group selected from alkyl, aryl and cyclohexyl, which groups may themselves be substituted with 1–3 substituents different from the said group and independently selected from hydroxy, alkoxy, aryl, aryloxy, cyclohexyl, cyclohexoxy, furyl (C_4H_3O), aroyloxy, alkoxy-carbonyl, alkanoyloxy, SO_2NH_2, $SO_2NHaryl$, $SO_2NHalkyl$, $SO_2N(alkyl)_2$, NHCOOalkyl, SO_3M, alkyl-SO_3M, NHCONHalkyl, acylamido, alkylsulfonamido, succinimido ($C_4H_4O_2N$), glutarimido ($C_5H_6O_2N$), phthalimido ($C_8H_4O_2N$), 1-(2-pyrrolidono) (C_4H_6ON), cyano, $CONH_2$, CONHalkyl, $CON(alkyl)_2$, alkoxyalkoxy, alkylthio, halogen, arylthio, alkylsulfonyl and arylsulfonyl, R_2 and R_3 are each independently selected from H and alkyl, R_4 is H, alkyl or alkyl-SO_3M, and R_5 is selected from H, alkyl, alkoxy, alkenyl of 2–6 carbons, halogen, acylamido, alkylthio and formamido, wherein the alkyl moieties thereof may be substituted with 1–3 substituents independently selected from hyroxy, halogen, cyano, alkoxy, alkylthio, alkanoyl, alkanoyloxy, and alkoxycarbonyl.

3. A dye according to Claim 2 wherein the substituents on the D rings are selected from alkylthio, arylthio, cyclohexylthio, alkyl-SO_3M, cyanoalkyl, alkyl and halogen, R_1 is H, alkyl, hydroxyalkyl, alkanoyloxyalkyl or alkoxycarbonylalkyl, and R_5 is H or alkyl.

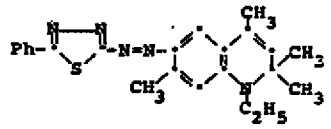
4. The dye according to Claim 1 of the formula



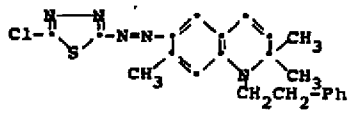
5. The dye according to Claim 1 of the formula



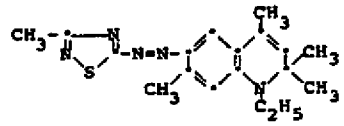
6. The dye according to Claim 1 of the formula



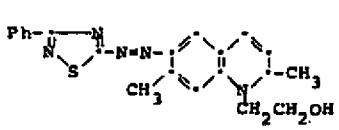
7. The dye according to Claim 1 of the formula



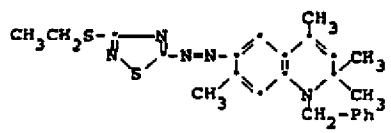
8. The dye according to Claim 1 of the formula



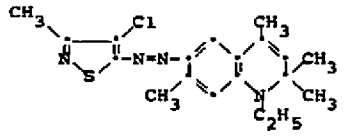
9. The dye according to Claim 1 of the formula



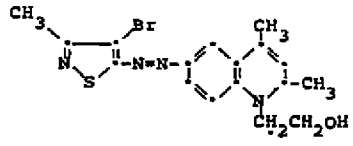
10. The dye according to Claim 1 of the formula



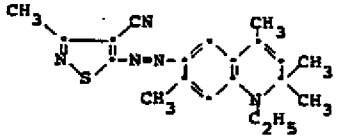
11. The dye according to Claim 1 of the formula



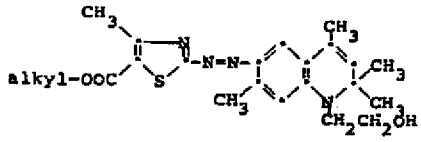
12. The dye according to Claim 1 of the formula



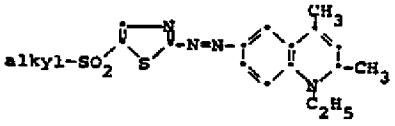
13. The dye according to Claim 1 of the formula



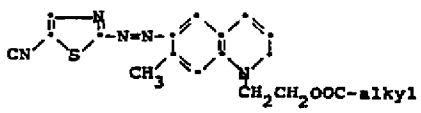
14. The dye according to Claim 1 of the formula



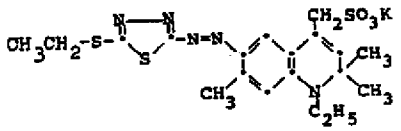
15. The dye according to Claim 1 of the formula



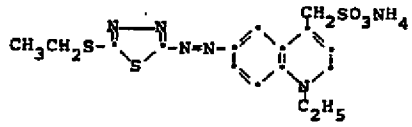
16. The dye according to Claim 1 of the formula



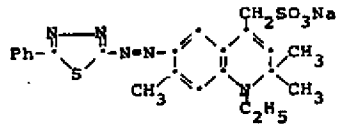
17. The dye according to Claim 1 of the formula



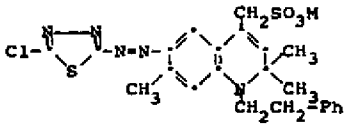
18. The dye according to Claim 1 of the formula



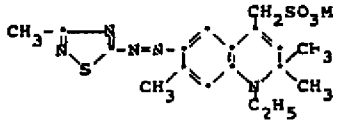
19. The dye according to Claim 1 of the formula



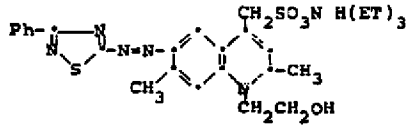
20. The dye according to Claim 1 of the formula



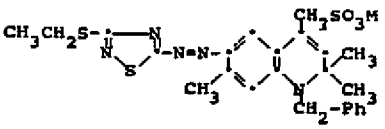
21. The dye according to Claim 1 of the formula



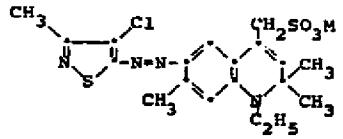
22. The dye according to Claim 1 of the formula



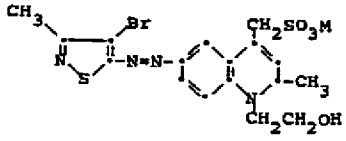
23. The dye according to Claim 1 of the formula



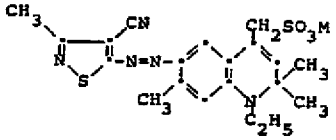
24. The dye according to Claim 1 of the formula

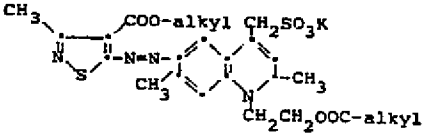


25. The dye according to Claim 1 of the formula

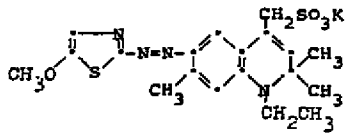


26. The dye according to Claim 1 of the formula

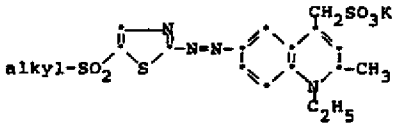




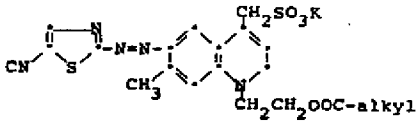
27. The dye according to Claim 1 of the formula



28. The dye according to Claim 1 of the formula



29. The dye according to Claim 1 of the formula



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